SECTION 5.0
EMISSIONS FROM MAJOR USES OF BENZENE

The largest portion of benzene produced is used in the production of ethylbenzene/styrene. Other major chemicals for which benzene is used as a feedstock include cyclohexane, cumene, phenol, nitrobenzene, and linear alkylbenzene. For each of these emission sources, the following information is provided in the sections below: (1) a brief characterization of the national activity in the United States, (2) a process description, (3) benzene emissions characteristics, and (4) control technologies and techniques for reducing benzene emissions. In some cases, the current Federal regulations applicable to the source category are discussed.

Emission factors are presented, as available. The reader is advised to contact the specific source in question to verify the nature of the process, production volume, and control techniques used before applying any of the emission factors presented in this report.

Other minor chemicals where benzene is used as a feedstock include resorcinol, benzophenone, hydroquinone, anthraquinone, biphenyl, and benzene sulfonic acid.[68] These chemical processes are discussed briefly in this section. Although benzene has been used in the past as a feedstock in the production of maleic anhydride, all capacity for producing maleic anhydride in the United States is now n-butane based; therefore, the process for producing maleic anhydride from benzene is not included in this section.

5.1 ETHYLBENZENE AND STYRENE PRODUCTION

Ethylbenzene is a liquid at standard conditions, with a boiling point of 277 °F (136°C) and a vapor pressure of 1,284 Pa (0.0126 atm).[69] About 50 percent of the U.S. production of benzene is used to produce ethylbenzene. The ethylbenzene industry is closely tied to the styrene industry because styrene is produced exclusively from ethylbenzene. There can be approximately a 0.3 percent by weight carry-over of benzene into ethylbenzene and styrene.[9] Additionally, some benzene is reformed in the production of styrene. Ethylbenzene production processes and uses thereby constitute a major potential source of benzene emissions, particularly because styrene production is anticipated to experience continued growth. Ethylbenzene demand is expected to show growth of only 2.5 to 3.5 percent per year over the next several years.[70]

Ethylbenzene is used almost exclusively to produce styrene. Some ethylbenzene is used as a solvent (often replacing xylene) and in the production of some dyes.[71] Total ethylbenzene production capacity is currently 13,874 million pounds per year (lb/yr) (6,293 kg/yr).[11] Approximately 95 percent of this capacity is based on benzene alkylation, with the remainder based on extraction from mixed xylene streams. Most styrene is produced by two methods: hydrogenation of ethylbenzene (89 percent) and peroxidation of ethylbenzene with subsequent hydration (11 percent). The latter process can also co-produce propylene oxide. A third process, converting ethylbenzene isothermally to styrene, was developed in Europe. To date, no U.S. facilities report using this method.

Another method that co-produces both ethylbenzene and styrene has been patented.[72] In this process, toluene and light alkanes other than ethane are reacted at 1,832 to 2,192 °F (1,000 to 1,200°C) and then gradually cooled to produce an 80 percent ethylbenzene/12 percent styrene product with a mass of about 25 percent by weight of the toluene reactant. These products can be separated by distillation, and the ethylbenzene either recycled, sold, or converted to styrene by another process--dehydrogenation or peroxidation. This process is not reported to be in use at this time.

Table 5-1 lists U.S. producers of ethylbenzene and styrene.[11,69,73] Most facilities produce both ethylbenzene and styrene on site, thus reducing shipping and storage. Only one styrene production site does not have ethylbenzene production capacity. Four ethylbenzene production sites do not have styrene production capacity. Ethylbenzene from mixed xylene separation is generally shipped or supplemented with another ethylbenzene source for styrene production. Only one site uses the peroxidation process to produce styrene. Table 5-1 also gives the latest facility capacity.

5.1.1 Process Description for Ethylbenzene and Styrene Production Using Benzene Alkylation and Ethylbenzene Dehydrogenation

Most ethylbenzene production is integrated with the dehydrogenation process to produce styrene; therefore, these processes are described together. The primary reactions are (1) catalytic alkylation of benzene with ethylene to produce ethylbenzene, and (2) catalytic dehydrogenation of ethylbenzene to produce styrene.

A process flow diagram including the basic operations that may be used in the production of ethylbenzene by benzene alkylation with ethylene is shown in Figure 5-1.[14,74]

The first step in the process is the drying of benzene to remove water from both feed and recycled benzene. An emission source in this process is the vent from the benzene drying column (Vent B).[69]

The dry benzene (Stream 1) is fed to the alkylation reactor along with ethylene, aluminum chloride catalyst, and recycled polyethylbenzenes. The reactor effluent (Stream 2) goes to a settler, where crude ethylbenzene is decanted and the heavy catalyst-complex layer is recycled to the reactor. Any inert gases fed with the ethylene or produced in the alkylation reactor, along with some unreacted benzene, other organics, and hydrogen chloride, are exhausted from the reactor or from the treating section (Vent A). Reactor vent gas is generally routed through a condenser and scrubbers in the alkylation reaction section (not shown on the

TABLE 5-1. U.S. PRODUCERS OF ETHYLBENZENE AND STYRENE

		Ethylbenzene		Styrene	
Company	Location	Process	Capacity million lb (million kg)	Process	Capacity million lb (million kg)
Amoco Chemical Company	Texas City, TX	NA	908[a] (412)	C[b]	800[a] (363)
ARCO Chemical Company	Channelview, TX	NA	2789[a] (1265)	D[b]	2525[a] (1145)
	Monarca, PA		220 (100)	---	---
Chevron Chemical Company	St. James, LA	NA	1700[a] (771)	C[b]	1525[a] (692)
Cos-Mar, Inc.	Carville, LA	A[c]	2200[a,d] (998)	C[b]	1900[a] (862)
Deltech Corporation	Baton Rouge, LA	NA	694[a,e] (315)	---	---
Dow Chemical U.S.A.	Freeport, TX	A[c]	1750[a] (794)	C[b]	1420[a] (644)
Huntsman Chemical Corporation	Bayport, TX	NA	1240[a] (562)	C[b]	1250[a] (567)
Koch Refining Company	Corpus Christi, TX	65% A[c] 35% B[c]	100[a] (45)	---	---
Phibro Energy USA, Inc.	Houston, TX	NA	25[a] (11)	---	---
Rexene Corporation	Odessa, TX	NA	350[a] (159)	C[b]	320[a] (145)
Sterling Chemicals, Inc.	Texas City, TX	NA	1750[a] (794)	C[b]	1600[a] (726)
Westlake Styrene Corporation	Lake Charles, LA	NA	368[a] (167)	---	---
	Sulphur, LA	---	---	C[b]	353[a] (160)

(continued)

TABLE 5-1. CONTINUED

Source: References 11, 69, and 73.

[a]Reference 11.
[b]Reference 73.
[c]Reference 69.
[d]Capacity does not include an excess capacity of 500 million pounds (227 million kg) of capacity on standby.
[e]Plant is on standby.

NA = Not available.

A = Benzene Alkylation (ethylbenzene production)
B = Xylene Separation (ethylbenzene production)
C = EB Hydrogenation (styrene production)
D = EB Peroxidation and Dehydration (styrene production)

"--" = means that the plant does not make this product.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contact with plant personnel. These data for producers and locations were current as of January 1993.

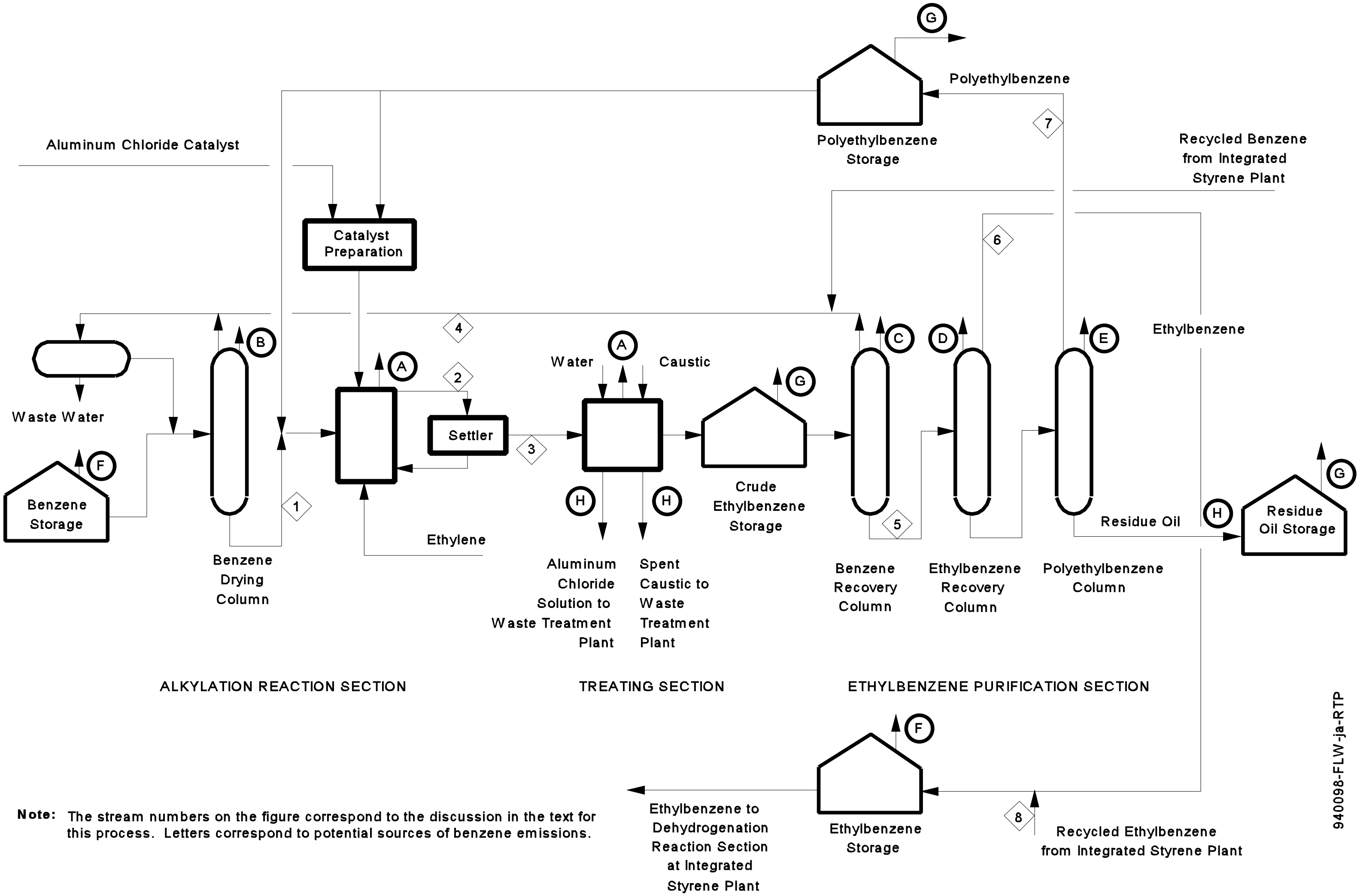

Figure 5-1. Basic Operations that may be used in the Production of Ethylbenzene by Benzene Alkylation with Ethylbenzene

Source: References 14 and 74.

figure) to recover aromatics and to remove hydrogen chloride (HCl) before the remaining inert gases are vented.[69]

The crude ethylbenzene (Stream 3) from the settler is washed with water and caustic to remove traces of chlorides and then fed to the ethylbenzene purification section. The crude ethylbenzene contains 40 to 55 percent benzene, 10 to 20 percent polyethylbenzene (PEB), and high-boiling point materials. The first step in purification is separation of recycled benzene (Stream 4) from the crude ethylbenzene in the benzene recovery column. In the second step, the product ethylbenzene (Stream 5) is separated from the heavier hydrocarbons in the ethylbenzene recovery column. The heavier hydrocarbons are distilled in the polyethylbenzene column to separate the polyethylbenzenes, which are recycled (Stream 7), from the residue oil.[69] Emission points in the purification section include vents from the benzene and ethylbenzene recovery columns (Vent C and D, respectively) and the polyethylbenzene column (Vent E).[69]

Fresh ethylbenzene (Stream 6) from the ethylbenzene purification section is combined with recycled ethylbenzene (Stream 8) from the styrene purification section at the integrated styrene plant and is stored for use as an intermediate for making styrene.[69] Other emission points from the process including storage tanks, are shown in Figure 5-1.

A process flow diagram including the basic operations that may be used in the production of styrene by ethylbenzene dehydrogenation is shown in Figure 5-2.[69,74]

Fresh ethylbenzene from the ethylbenzene purification section (ethylbenzene plant) is combined with recycled ethylbenzene (Stream 1) from the styrene purification section. The purified ethylbenzene is preheated in a heat exchanger. The resultant vapor (Stream 2) is then mixed continuously with steam at 1,310°F (710°C) in the dehydrogenation reactor, which contains one of several catalysts. The reaction product (Stream 3) then exits through the heat exchanger and is further cooled in a condenser, where water and crude styrene vapors are condensed.